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Measurement of non-linear optical coefficients of chalcogenide glasses near the fundamental absorption band edge

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ABSTRACT

A time-resolved pump-probe method is used for the evaluation of non-linear optical coefficients of chalcogenide glasses from the As-S-Se and Ge-Se systems near their fundamental absorption band edges. The results are analyzed via comparison with the spectral dependencies of the non-linear optical coefficients of crystalline semiconductors; the role of electron transitions through the gap states of chalcogenide glasses is discussed.

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(190.4400) Nonlinear optics, materials; (160.2750) Glass and other amorphous materials; (320.2250) Femtosecond phenomena

1. Introduction

The non-linear optical response of chalcogenide glasses has been studied experimentally for the past 20 years. It was found that non-linear optical coefficients concerning to the third-order non-linear polarization were 2–3 orders greater than those of fused silica. As the optical bandgap energy E_g of a chalcogenide glass composition is usually <2.5 eV [1] their fundamental absorption band (FAB) edges correspond to the bandgap wavelengths $\lambda_g > 0.5$ μm. In fact, non-linear optical coefficients of the glass systems As-S-Se, Ge-Se, Ga-La-S and others have been measured mainly at the wavelengths λ: 1.064 μm, 1.25 μm and 1.55 μm of available ultra-fast lasers [2]. At these wavelengths, the ratio $R_e = h\nu / E_g$ ($h\nu$ is the laser photon energy) is <0.6. Meanwhile, the range $0.6 < R_e < 1$ is of current interest in both fundamental and applied research.

In the technology of waveguides inscription in optical glasses, the non-linear coefficients of refraction and absorption are basic parameters, which govern a high-intensity laser pulse energy deposition into a glass sample and final refractive index variation. When illuminated in a spectral range near the FAB edge, chalcogenide glasses exhibit specific photo-structural changes known as photodarkening [1]. The character of the non-linear optical response in a chalcogenide glass sample depends on whether the sample has been illuminated near to or far from the FAB edge [3].

Up to now, a theory of the non-linear optical response of non-crystalline semiconductors, in particular, chalcogenide glasses, has not been developed. In the theory of crystalline semiconductors, a two-band model [2,4,5] is usually used to describe the third-order non-linear polarization. However, this model is incompatible with non-crystalline semiconductors that have energy levels in their bandgaps (so called gap states). Nevertheless the theory of crystalline semiconductors was used in some papers for evaluation of the non-linear optical coefficients of refraction n_2 and absorption β_2 of chalcogenide glasses [6–9]. (These coefficients correspond to the intensity-dependent parts of the refractive index $n = n_0 + n_2 I$ and absorption coefficient $\alpha = \alpha_0 + \beta_2 I$, where n_0 and α_0 are, respectively, the linear refractive index and single-photon absorption coefficient, and I is intensity of the laser radiation.) Far from the FAB edge, when $\lambda > \lambda_g$, comparison of the theoretical values with experimental data provides some fit [7], but there is a discrepancy near the FAB edge because in the theory of the direct-gap crystalline semiconductors, n_2 is negative-valued over some part of the spectral range ($R_e > 0.7$) [4]. Meanwhile in accordance with

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the available experimental data [2], only $n_2 > 0$ has hitherto been observed in all the range of transparency of chalcogenide glasses.

In experiments on n_2 and β_2 measurements near the FAB edge, densities of photo-excited charge carriers in a sample can be large due to the single- and two-photon absorption. This effect can significantly violence the output parameters especially when laser pulses of nano- or pico-second durations are used for pumping [10].

In this work, a time-resolved pump-probe method was applied to evaluate n_2 and β_2 of chalcogenide glasses from the As-S-Se and Ge-Se systems near their FAB edges. In the experiment, a single femtosecond (fs) pump pulse was used for a glass sample illumination at each probe pulse delay. To avoid a cumulative effect, the sample was moved after each shot. Together with a thorough analysis of the short time scale dynamics of the non-linear optical response, this enabled us to realize the experimental conditions when the photo-excited free electrons density is small and can be neglected in a numerical model used for n_2 and β_2 evaluation.

2. Experiment

Samples of the compositions $As_{40}S_xSe_{60-x}$ (x = 0, 15, 30, 45, 60) (atomic %) and $Ge_{20}Se_{80}$, $Ge_{12}Se_{88}$ were fabricated from synthesized glass rods, shaped as thin disks (thickness ~1 mm) and polished to a 0.25 μm finish [11]. The FAB edges in absorption spectra obtained from spectrophotometric measurements [11,12] are shown in Fig. 1. The linear part of each curve corresponds to the Urbach tail [1]. The weak absorption tails (WAT) typically refer to the range where $\alpha_0 < 1\ cm^{-1}$. These glass samples were illuminated by laser pulses (HMFW duration $\tau = 50$ fs) with the peak wavelength $\lambda^p = 0.79$ μm ($h\nu^p = 1.57$ eV).

Fourier Transform interferometry [13] enabled us to measure the non-linear optical response of these glass samples with femtosecond resolution in time. In the experiment, a high intensity pump pulse was focused onto a sample by a lens with a focal distance of 300 mm after a 3 mm aperture (a schematic of the experimental set-up is shown as the inset to Fig. 2). The sample was moved after each shot. A probe pulse propagating with some delay Δt after the pump pulse was divided into two pulses at a Michelson interferometer. As the probe beam diameter was several times greater than the pump beam diameter, after the interferometer a disturbed central part of one probe beam overlapped with an unexcited peripheral part of the other one. An interference pattern was recorded at the spectrometer exit and finally a Fourier Transform was performed to extract the phase shift $\Delta\varphi$ of the probe pulse at each transverse coordinate for each Δt. The magnitude and sign of $\Delta\varphi$ induced due to the effect of cross-phase modulation were proportional to the variation of the real part of the refractive index upon the pump pulse illumination.

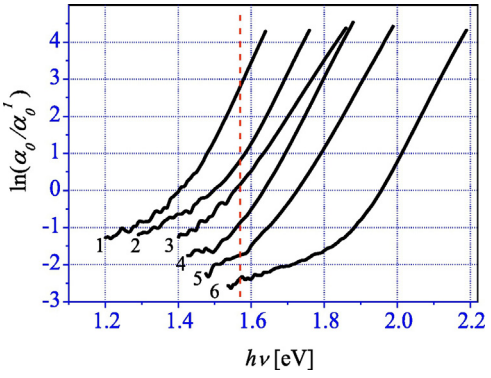

Fig. 1. Logarithm of the absorption coefficient of the glass compositions $As_{40}S_xSe_{60-x}$, x = 0 (1), 15 (2), 30 (4), 45(5), 60 (6) and $Ge_{20}Se_{80}$ (3). The vertical dashed line indicates $h\nu^p = 1.57$ eV. $\alpha_0^1 = 1\ cm^{-1}$.

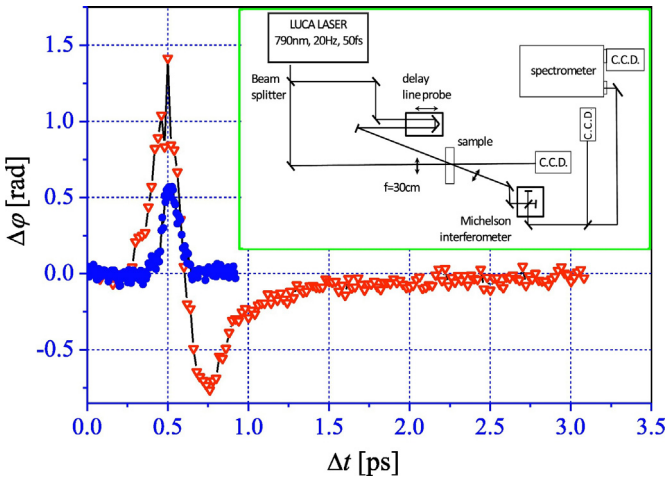

Fig. 2. Time-resolved non-linear optical response of the glass samples: $As_{40}S_{60}$, $E = 0.3$ μJ (filled circles), 9.2 μJ (open triangles); inset: the pump-probe set-up scheme.

It was proposed in [13] that the dielectric constant of a glass sample varies due to the third-order non-linearity, free charge carriers excitation and their trapping at the gap-states. This can be observed in Fig. 2, which displays the time dependence of $\Delta\varphi$ averaged over the probe beam cross-section for the sample $As_{40}S_{60}$. At low pulse energy E (see the curve $\Delta\varphi(\Delta t)$ at $E = 0.3$ μJ in Fig. 2, filled circles), the dielectric constant changes predominantly due to the third-order non-linearity (optical Kerr effect) and this reveals itself as a positive-valued maximum in $\Delta\varphi(\Delta t)$. At higher E (the curve $\Delta\varphi(\Delta t)$ at $E = 9.2$ μJ in Fig. 2, open triangles), this maximum is followed by a fast $\Delta\varphi$ decrease down to negative values due to the photo-excitation of free electrons. At greater Δt, a subsequent slow increase in $\Delta\varphi$ magnitude is observed; this is assumed to be due to the charge carriers recombination (followed by a permanent change of refractive index at $\Delta t > 4$ ps [3]). In chalcogenide glasses, the kinetics of charge carriers develops as both radiative and non-radiative recombination [14].

At low E, when the density of photo-excited electron-hole pairs is negligibly small, the propagation of the laser pulses in the sample along the z – direction, normal to the sample surface, is described by the equations:

$$\partial I_{pu}/\partial z = -(\alpha_0 + \beta_2 I_{pu}) I_{pu} \tag{1a}$$

$$\partial I_{pr}/\partial z = -(\alpha_0 + 2\beta_2 I_{pu}) I_{pr} \tag{1b}$$

$$\partial \phi_{pu}/\partial z = k n_2 I_{pu} \tag{1c}$$

$$\partial \phi_{pr}/\partial z = 2k n_2 I_{pu} \tag{1d}$$

where $I_{pu}(r,z,t)$ and $I_{pr}(r,z,t)$, $\varphi_{pu}(r,z,t)$ and $\varphi_{pr}(r,z,t)$ are, respectively, the pump and probe pulse intensities and their phases; r is the transverse coordinate, t is the time in the moving frame coordinate system, and $k = 2\pi / \lambda^p$. The Eqs. (1a), (1b), (1c), (1d) do not include any derivatives with respect to the transverse coordinate r because at low E, we have found that the laser beam spot size in the sample did not vary significantly with Δt. A small angle between the pump and probe pulses equal to 18.5° in air (<7° in a sample) was also not taken into account.

From Eqs. (1a), (1b), (1c), (1d), the following expressions for evaluating n_2 and β_2 have been obtained:

$$\beta_2 = \left(1 + (1-A)^{-1/2}\right) / \left(I_{pu}^0 L^{(\alpha)} \left(1 + (L/L_d)^2\right)^{-1/2}\right) \tag{2}$$

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